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EMPLOYING NEUTRON ACTIVATION ANALYSIS

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PROVENIENCE STUDIES OF TEL ASHDOD POTTERY
EMPLOYING NEUTRON ACTIVATION ANALYSIS

I. Perlman*, Frank Asaro*, and J. D. Friermant

There is evidence that pottery made from different clay sources will reveal differences in composition if subjected to sufficiently detailed chemical analysis. The profile of abundances of elements of a ceramic vessel can thus serve as a "fingerprint" relating it to its place of origin. For reasons which need not be elaborated here, the only feasible types of analysis are those which can determine many elements simultaneously and which are sensitive enough to measure accurately a considerable number of those present only in trace amounts. A method which meets these criteria is called neutron activation analysis.¹

When any substance such as pottery is exposed to neutrons in a nuclear reactor, the various elements therein give rise to radioactive forms each of which emits unique radiations. In principle, these can be measured with suitable electronic equipment and the results eventually related quantitatively to the amounts of the individual elements responsible for their creation. The sensitivity of the measurement varies considerably for different elements and, indeed, for some elements the method is not practicable. Nevertheless, a system has been worked out for measuring more than 30 elements in pottery without resorting to chemical fractionation in the laboratory. Only about 100 mg. of powdered pottery is used for each analysis.

The radiations most suitable for such general analyses are the gamma-rays which accompany radioactive decay in most of the unstable species produced in neutron activation. Only in recent years, however, has equipment been developed with sufficiently high resolution to discriminate between the huge number of gamma-rays found in irradiated pottery.

There are at present no a priori guidelines for interpreting the analytical data, so inferences are drawn in part from archaeological information. A group of sherds are selected which are almost certainly local materials and in an ideal case the abundances of each of the various elements will be similar. The mean values of the respective elements and their standard deviations make up the chemical composition profile of the pottery group. Any other sherd may then be compared with this group by statistical methods in order to determine whether it belongs to the group. Complexities arise when more than one pottery

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¹ A number of studies have appeared in the literature applying neutron activation to pottery analysis. The reader is referred to one of these which is a detailed description of the methodology and an assessment of the accuracy attainable (1).

group arise in the "local" material. Unless a large number of analyses are done, it is not possible to know for sure whether some of these are imports or whether they represent different clay sources used by the local settlement. However, the information obtained is accumulative and as the library of chemical types grows, more and more can be said about their exact point of origin.

The results presented here concern a small collection of sherds from Tel Ashdod which are expected to be the forerunner of a more detailed analysis of the site. The collection comprises only five "local" Philistine sherds, four of Cypriote White Slip II Ware and two Mycenaean III B pieces. These pieces are surface finds (or of unstratified context) but are well correlated through stratified counterparts: Philistine sherds - mainly Stratum XII; Cypriote and Mycenaean sherds - mainly XV and XIV.

PHILISTINE WARE

In Table I are shown analytical results on 18 elements for the five Tel Ashdod Philistine sherds. These particular elements (among the larger number determined) are used in the statistical analysis because there is some evidence that they may be treated as independent variables in defining the composition profile of a pottery group. Particular attention is called to the "error limits" employed. The limits shown on the elemental abundances for the individual sherds are the standard errors of the respective measurements. Each entry in parentheses is the mean value for an element in the pottery group and the standard deviation (σ) encountered in the group for that element. These latter numbers are used to determine whether any sherd belongs to the group.

No justification has yet been given for classifying these sherds as a "pottery group" other than the usual archaeological arguments. The potential usefulness of the chemical analysis lies, of course, in the proposition that this system is independent of archaeological criteria. Unfortunately, there are no a priori guidelines delineating the range of compositions to be expected from a single source and only the examination of a large number of specimens from many sites can lead to confidence in making such groupings. Based on some such experience, we have adopted tentative statistical criteria which may well have to be revised as further experience is gained. Without elaborating on this subject, we shall simply state that the group of Tel Ashdod Philistine sherds shown in Table I make up about as compact a chemical pottery group as we have yet encountered.

The second set of data shown in Table I pertain to five pieces of Philistine pottery excavated from tombs at Tel Eitun.² Only the mean values with their standard deviations are shown for this group. (Ten other pieces from Tel Eitun were analyzed but none of these belong to this particular group.) When this Tel Eitun group is compared statistically with that from Tel Ashdod, they are found to be indistinguishable. The straightforward conclusion that these five particular tomb finds from Tel Eitun actually came from Tel Ashdod must be approached with some

²We are indebted to Dr. Gershon Edelstein for providing the Tel Eitun material and wish to thank him for his permission to use these results in the present publication.

caution.

In the first place, we should like to analyze a much larger collection than five sherds from Tel Ashdod to be sure that these are representative of material from that site. Logically, these five sherds could as well have come from Tel Eitun or both groups could have come from some other place. The arguments against this open-ended interpretation are (1) different chemical types were found at Tel Eitun and one of these could represent local materials, and (2) there is some independent evidence that the five Tel Eitun vessels in question are of coastal clays.³ The second word of caution has to do with the lack of proof that the composition of Tel Ashdod Philistine pottery is unique. It is possible that in some regions of the world, clay sources at different sites share a virtually identical geochemical background and are the same in composition. In order to establish firmly that Tel Ashdod is indeed the source of this pottery, one must analyze pottery from a number of other coastal sites.

To provide contrast with the above mentioned materials, Table I also shows results on two Philistine vessels from Tel Eitun of a different chemical type (ETN3 and ETN13). Of the major constituents, it is seen that the calcium content of these is considerably higher and the iron appreciably lower. Most of the trace elements are also well outside of the standard deviations of the reference materials. The quantitative nature of the disagreement may be mentioned although we are not completely satisfied as to the proper method of handling the statistical analysis. If we assume that the five Tel Ashdod and five Tel Eitun pieces constitute a single chemical group, then the odds that ETN3 and ETN13 belong to this group are only 1 in 10^{35} . Such large numbers are, of course, very convincing but the exact magnitude should not be taken literally because the statistical analysis based on so many elements is extremely sensitive and the assumption that the individual elements may be treated as independent variables can probably not be firmly established.

CYPRIOTE WARE

The results for the Cypriote White Slip II Ware (four sherds) are tabulated as the upper group in Table II. These do not by any means make up a close-knit pottery group but they share some characteristics which make them highly distinctive. Although we cannot refer to a typical chemical pottery type, this Cypriote ware has extreme divergences for a number of elements from values obtained on a large variety of pottery analyzed from many sites. This particular Cypriote ware, for example has the lowest values yet seen anywhere for U, La, Hf, Th, and Rb; at the same time they have about the highest values for Fe and Sc.

We have begun a rather ambitious program of analyzing pottery excavated on Cyprus, embracing major stylistic types from 11 sites.⁴ The same distinctive chemical profile as the Tel Ashdod material has turned up but we are not yet ready to attempt the determination of the

³A private communication from Dr. Edelstein refers to a mineralogical examination of these Tel Eitun vessels by Mr. Jonathan Glass. He states that these particular Tel Eitun pieces have quartz inclusions which he believes are characteristic of coastal clays.

⁴This study is being carried out in collaboration with Professor Einar Gjerstad of the University of Lund. We wish to thank him as well as Dr. Olof Vessberg of Mediterranean Museum, Stockholm, for providing the large collection of Cypriote ware.

exact place of origin. Not enough sites have yet been examined and where this has been done several different pottery groups are emerging all with the same general characteristics of the White Slip Ware described above. One such "group" from Ayios Jakovos is shown in summary form in Table II. This "group" consists of seven sherds but it is possible that they all came from only two vessels. They were treated as seven independent pieces because for the purposes of comparison shown here, it would make little difference whether they were treated as seven or two.

The agreement between this group and the Cypriote sherd ASH5 is very good. Other ware from Ayios Jakovos as well as from Enkomi and Milia is of this same distinctive chemical type and illustrations could be given which encompass the compositions of the other Cypriote pieces from Tel Ashdod. Pottery of this style from still other sites on Cyprus have not yet been available for analysis.

One conclusion is unmistakable. Wherever the various groups of White Slip Ware may have been made, the potters selected a particular type of clay for this ware because other styles of Cypriote ware were distinctly different in chemical composition. No White Slip Ware was made of dominant clay types used for other pottery styles and only rarely have other styles been encountered which were made from this distinctive type of clay. Since we have only sampled a limited geographical area, it is possible, of course, that all of the White Slip Ware encountered came from some localized set of potters' shops drawing clay from a set of pits in the vicinity. Analyses on a wider range of White Slip Ware from Cyprus and elsewhere should help clear up this point. For the present, we can only say that the Tel Ashdod White Slip Ware is of a distinctive composition thus far only encountered in eastern Cyprus.

MYCENAEAN WARE

The two Mycenaean sherds, it will be shown, have their counterparts in materials already analyzed in our laboratory but their exact interpretation is beclouded by some puzzling features of these reference materials. The difficulties will be explained presently and it will become clear that no definitive answers will be forthcoming until a program is undertaken to characterize Mycenaean pottery from a wide range of sites.

The two sherds from Tel Ashdod are from bowls or kraters classified LM III B. The results for the individual pieces are given in Table III. The Mycenaean reference materials are sparse, consisting of a small collection of five sherds. Three of these are said to come from Mycenae and two from the island of Kea. One of the Kea pieces (described as an import) along with the three Mycenaean pieces made up a fairly compact chemical group and results in summary form are presented in Table III. The other piece from Kea is quite different and since nothing further can be said about it at present, the results are not tabulated.

Of the two pieces from Tel Ashdod, one of them (ASH 12) matches the reference group better than would be expected of a member of a normal statistical array. Eighteen elements are tabulated and only the value for chromium falls outside (slightly) of one standard deviation from the reference group value. In view of the few number of sherds

defining the reference group, it is not profitable to speculate on the reason for this unusual agreement. Mathematically, however, this behavior signifies that the composition of ASH 12 is closer to the mean composition of the reference group than are the individual members of that group.

The other sherd, ASH 3, is made from a closely similar clay but it does not quite "belong" to the reference group. Again, in view of the meagerness of the collection with which we are dealing, it is not possible to ascribe a different provenience to this sherd.

The large difficulty in the interpretation of these materials at present is the following: It seems rather puzzling that six out of seven Mycenaean III B found in three different places have proved to be close enough alike to be classed as a group. A hasty explanation is that all of these have a common place of origin. However, one must also consider the possibility that they came from more than one place but that the clay sources are indistinguishable by our analysis. As already alluded to, a much more ambitious effort must be undertaken before questions of origin of Mycenaean pottery can be answered.⁵

CONCLUSIONS

The analysis of this small collection of Tel Ashdod sherds has yielded no surprises but suggests that a much amplified study could help provide a detailed picture of contacts between this settlement and others in the vicinity and at a distance.

The Philistine sherds of Level XI have chemical counterparts in a group found in tombs at Tel Eitun suggesting (but not yet proving) a common origin. Other Philistine pieces found at Tel Eitun were different. The Cypriote White Slip II sherds were not homogeneous but belong to a highly-distinctive type of clay so far found only in similar ware from three tomb sites in eastern Cyprus. Two sherds of Mycenaean III B ware were similar to each other and to a small collection of typologically similar ware said to have been excavated at Mycenae and also one sherd found on Kea. The Mycenaean reference materials in particular are too meager to draw firm inferences about the uniqueness of assignment.

For those unfamiliar with viewing analytical data of the kind shown in this paper, it is perhaps worth calling attention to the large differences in composition between the Philistine, Cypriote and Mycenaean ware illustrated in the Tel Ashdod material. The distinctions we have been trying to make in judging the provenience of the respective wares are miniscule compared with the differences between the different wares.

⁵Attention is called to an earlier and comprehensive study of Mycenaean ware by Catling, Richards and Blin-Stoyle (2) attempting to relate provenience and chemical composition. These authors employed spectroscopic analysis and unfortunately we cannot yet compare our results with theirs.

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Table I. Philistine Pottery from Tel Ashdod and Tel Eitun.

Code *	Fe (%)	Sc	Ta	Co	Cs	Cr	Hf	Th
ASH 1	3.80±0.04	12.42±0.04	1.195±0.048	17.59±0.27	1.49±0.18	122.0±1.2	10.58±0.19	7.13±0.05
ASH 4	3.84±0.04	12.66±0.04	1.166±0.046	19.30±0.29	1.61±0.19	119.2±1.2	12.75±0.21	7.84±0.05
ASH 6	3.89±0.04	13.01±0.04	1.263±0.050	19.20±0.30	1.58±0.19	120.8±1.3	12.89±0.21	7.83±0.05
ASH 8	3.83±0.04	12.76±0.04	1.187±0.051	18.97±0.30	1.86±0.20	128.3±1.3	16.48±0.26	8.58±0.06
ASH 10	3.96±0.04	13.12±0.04	1.189±0.046	20.43±0.29	1.65±0.18	129.9±1.3	14.44±0.23	9.04±0.05
Mean value								
ASH 1,4,6,8	(3.86±0.10)	(12.79±0.32)	(1.200±0.037)	(19.10±0.97)	(1.64±0.14)	(124.0±6.0)	(13.43±2.41)	(8.08±0.86)
Mean value								
ETN 1,6,7,9,14	(3.70±0.07)	(12.85±0.13)	(1.137±0.034)	(17.01±1.15)	(1.64±0.15)	(114.5±1.9)	(11.57±0.73)	(7.38±0.54)
ETN 3	3.01±0.03	10.72±0.03	0.857±0.031	13.43±0.15	1.24±0.12	118.8±0.9	7.75±0.12	6.12±0.04
ETN 13	3.10±0.03	10.66±0.02	0.856±0.028	13.41±0.14	0.88±0.10	125.2±0.9	8.13±0.13	5.95±0.04

All abundances of elements are in parts-per-million except those designated "%". Numbers in parentheses are mean values for the group of the standard deviations for the group. The other numbers refer to individual measurements and the standard errors of the gamma-ray counting only. Other errors of the measurements will add to these errors as explained in Ref. 1.

Table II. Cypriote Pottery from Tel Ashdod and Ayios Jakovos (Cyprus).

Code *	Fe (%)	Sc	Ta	Co	Cs	Cr	Hf	Th
ASH 2	6.23±0.06	36.39±0.07	0.353±0.056	34.44±0.45	0.69±0.29	181.5±1.8	2.22±0.18	2.52±0.06
ASH 11	7.09±0.06	40.00±0.08	0.423±0.056	37.29±0.48	0.74±0.36	202.4±2.0	2.17±0.19	2.61±0.07
ASH 5,9 **	7.74±0.05	41.30±0.05	0.192±0.032	46.10±0.35	0.35±0.18	260.7±1.4	1.77±0.11	1.91±0.04
ASH 7	7.09±0.06	46.39±0.07	0.346±0.037	52.99±0.51	0.90±0.23	839.6±5.2	1.83±0.13	3.03±0.05
Mean value								
JAK 9,12,14,15, 17,18,20†	(8.02±0.48)	(41.30±1.36)	(0.254±0.063)	(44.37±2.27)	(0.75±0.32)	(242.2±51.1)	(1.67±0.31)	(1.70±0.07)

* All pieces designated ASH are Cypriote White Slip II Ware from Tel Ashdod; those designated JAK are similar ware from Ayios Jakovos, Cyprus. Mean values are not given for the Tel Ashdod pieces because they cannot be placed in a group even though they share certain distinctive characteristics.

Table III. Mycenaean Pottery from Tel Ashdod with Comparative Material.

Code *	Fe (%)	Sc	Ta	Co	Cs	Cr	Hf	Th
ASH 3	5.39±0.05	23.12±0.05	0.837±0.042	35.63±0.39	8.56±0.24	295.4±2.1	3.60±0.13	12.01±0.06
ASH 12	5.25±0.05	21.21±0.05	0.812±0.046	29.17±0.36	9.13±0.26	245.6±2.0	3.91±0.15	11.31±0.06
Mean value								
MYC 1,2,3,6	(5.21±0.23)	(21.84±1.36)	(0.769±0.066)	(30.74±2.01)	(9.42±0.40)	(229.4±16.6)	(3.60±0.51)	(11.19±0.63)

* ASH 3 and ASH 12 from Tel Ashdod are characterized as Late Mycenaean IIIB. MYC 2, 3, and 6 are similar ware said to come from Mycenae. MYC 1 is also similar and it is described as an import found on Kea. Another sherd from Kea is not included here and is different in composition.

Table I. Continued.

Ba	Rb	Sb	U	Lu	La	Ti (%)	Ca (%)	Mn	Na (%)
228±23	53±5	0.447±0.059	2.57±0.11	0.372±0.010	29.47±0.29	0.584±0.034	7.6±0.7	755±16	0.614±0.010
333±26	51±5	0.329±0.059	1.95±0.11	0.441±0.011	28.24±0.29	0.693±0.034	3.8±0.6	777±16	0.655±0.011
384±26	54±6	0.395±0.061	2.11±0.11	0.418±0.011	27.88±0.28	0.683±0.033	3.1±0.6	742±16	0.611±0.011
476±30	60±6	0.430±0.068	2.02±0.11	0.449±0.011	30.15±0.31	0.773±0.036	3.6±0.6	810±17	0.610±0.011
490±28	46±6	0.432±0.061	1.99±0.11	0.454±0.011	30.56±0.31	0.754±0.036	5.1±0.6	924±19	0.628±0.011
(382±121)	(53±5)	(0.407±0.053)	(2.13±0.26)	(0.427±0.038)	(29.26±1.42)	(0.697±0.079)	(4.6±2.0)	(802±77)	(0.624±0.021)
(549±206)	(53±2)	(0.357±0.064)	(1.52±0.10)	(0.410±0.021)	(27.92±1.14)	(0.667±0.024)	(5.2±1.1)	(733±48)	(0.668±0.088)
687±24	32±4	0.354±0.040	1.90±0.10	0.348±0.009	26.52±0.26	0.484±0.031	14.2±0.6	560±8	0.499±0.009
1148±33	43±4	0.414±0.059	2.07±0.10	0.388±0.009	26.57±0.27	0.443±0.030	13.9±0.6	595±7	0.554±0.008

* ASH 1, 4, 5, 8, 10 are Philistine pieces from Tel Ashdod; ETN 1, 6, 7, 9, 14 are Philistine pieces from Tel Eitun closely similar to the Tel Ashdod ware as explained in the text. ETN 3 and ETN 13 are Philistine pieces different in composition from the others in this table.

Table II. Continued.

Ba	Rb	Sb	U	Lu	La	Ti (%)	Ca (%)	Mn	Na (%)
142±40	30±8	0.493±0.097	0.73±0.15	0.340±0.012	9.01±0.21	0.407±0.029	2.5±0.5	779±16	1.131±0.016
87±44	19±8	0.469±0.108	0.78±0.15	0.300±0.012	8.48±0.21	0.427±0.029	2.0±0.5	875±19	1.149±0.016
101±25	36±4	0.524±0.060	1.19±0.11	0.309±0.009	5.66±0.14	0.376±0.020	1.6±0.4	1102±17	1.060±0.011
88±32	29±6	0.300±0.073	0.67±0.25	0.324±0.013	8.01±0.27	0.479±0.035	2.3±0.5	1020±22	0.745±0.012
(111±79)	(34±11)	(0.387±0.236)	(0.31±0.16)	(0.308±0.015)	(5.79±0.31)	(0.374±0.028)	(2.3±0.6)	(1193±36)	(1.223±0.135)

** ASH 5 and ASH 9 are two sherds analyzed separately but which proved to come from the same vessel. The values listed are mean values with standard errors of gamma-ray counting.

† As explained in the text, these seven sherds may have come from only two bowls but have been treated here as independent pieces. This "group" is closely similar to ASH 5, 9.

Table III. Continued.

Ba	Rb	Sb	U	Lu	La	Ti (%)	Ca (%)	Mn	Na (%)
307±31	150±9	0.695±0.072	2.22±0.16	0.390±0.012	34.95±0.37	0.496±0.038	9.2±0.7	1003±21	0.601±0.011
367±34	156±9	0.658±0.080	2.20±0.15	0.345±0.011	31.42±0.34	0.486±0.035	8.6±0.7	953±20	0.547±0.010
(359±14)	(161±15)	(0.789±0.238)	(2.34±0.34)	(0.362±0.013)	(32.59±2.31)	(0.485±0.076)	(9.0±2.0)	(945±52)	(0.419±0.186)